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(54) Title: COMPOSITION COMPRISING PHOSPHONIUM SALTS AND THEIR USE

(57) Abstract: The present invention provides homogeneous mixtures of saturated hydrocarbons and tetrahydrocarbylphosphonium salt ionic liquids. The present invention further provides a process for expelling a hydrocarbon, preferably a saturated hydrocarbon, from a homogeneous mixture comprising the hydrocarbon and a tetrahydrocarbylphosphonium salt ionic liquid, which process comprises adding to the homogeneous mixture sufficient water to cause the hydrocarbon and the phosphonium salt to form separate phases.



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## COMPOSITIONS COMPRISING PHOSPHONIUM SALTS AND THEIR USE

FIELD OF THE INVENTION:

The present invention relates to phosphonium salts, in particular their use as solvents for chemical reactions and to methods of recovering reaction products.

BACKGROUND OF THE INVENTION:

Ionic liquids provide an attractive alternative to traditional organic solvents for many chemical reactions. Ionic liquids are non-flammable, have low vapour pressure, high solvation abilities, are recyclable with low or no waste and have high E factor and low cost factor. Reactions in ionic liquids typically proceed under milder conditions at rates that are comparable or much faster as compared to conventional solvents. Also, as a result of their distinctive physical and chemical properties, ionic liquids can influence the stereoselectivity and regioselectivity of reactions. For industrial purposes, the low vapour pressure of ionic liquids is a very important feature. They are essentially non-volatile, a property that eliminates many of the containment problems typically encountered with traditional organic solvents. Also, since many of the ionic liquids are immiscible with traditional organic solvents, they offer a non-aqueous alternative to two-phase systems. Hydrophobic ionic liquids can also be used as immiscible polar phases with water.

Another important feature of ionic liquids is that they are good solvents for a wide range of both inorganic and organic compounds, and thus ionic liquids can be used to bring inorganic reactants (e.g. inorganic catalysts) and organic reactants into homogeneous solutions. The ability to combine reagents to form homogeneous solutions is

advantageous because reactions in homogeneous solutions are inherently more efficient than reactions performed in heterogeneous solutions. For example, when a catalytic reaction is carried out in a homogeneous solution, all of the metal centers of the catalyst are available to the reagents. Indeed, startling differences in yields and specificity have been seen between reactions in ionic liquids as compared to traditional solvents. A recent review of the properties and uses of ionic liquids is provided in an article entitled "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis," by Thomas Welton (Chem. Rev. 1999, 99, 2071-2083), the disclosure of which is incorporated herein by reference.

Imidazolium salts find utility as ionic liquid solvents. Imidazolium salts containing anions such as tetrafluoroborate and hexafluorophosphate anions are excellent solvents for many organic reactions. However, some of the commonly used imidazolium salts, such as 3-butyl-1-methylimidazolium hexafluorophosphate, may not support homogeneous reactions with nonpolar compounds, such as saturated hydrocarbons, because these compounds are not mutually miscible. For example, cyclohexane does not dissolve in 1-butyl-3-methylimidazolium hexafluorophosphate. Also, the miscibility of 1-pentene in 3-butyl-1-methylimidazolium hexafluorophosphate ([bmim]-PF<sub>6</sub>) is poor, and these two compounds exist in separate phases (see Example 1 in U.S. Patent No. 5,852,130 and Example 1 in U.S. Patent No. 6,040,263). Pentane would be even less miscible with [bmim]-PF<sub>6</sub> because pentane is less polar than 1-pentene.

Phosphonium salts may be used as ionic liquids and have thermal stabilities that are comparable to or greater than the corresponding imidazolium salts.

**SUMMARY OF THE INVENTION:**

In one aspect the invention provides a homogeneous mixture comprising a saturated hydrocarbon and a phosphonium salt. The invention also provides the use of a phosphonium salt as a solvent for a saturated hydrocarbon. The invention further provides a method for making a homogeneous solution comprising contacting a saturated hydrocarbon with a phosphonium salt.

In another aspect, the invention provides a homogeneous mixture comprising a metal catalyst, a saturated hydrocarbon and a phosphonium salt. The invention also provides the use of a phosphonium salt as a solvent for making a homogeneous mixture of a metal catalyst and a saturated hydrocarbon. The invention further provides a method for making a homogeneous solution comprising contacting a saturated hydrocarbon and a metal catalyst with a phosphonium salt.

In another aspect, the invention provides a process for expelling a hydrocarbon, preferably a saturated hydrocarbon, from a homogeneous mixture comprising the hydrocarbon and a phosphonium salt ionic liquid, which process comprises adding to the homogeneous mixture sufficient water to cause the hydrocarbon and the phosphonium salt to form separate phases.

The invention further provides a three phase liquid composition comprising a hydrocarbon phase, a phosphonium salt phase, and a water phase.

**DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION:**

Solvent polarity is commonly used to classify solvents. A simple qualitative definition says that a polar solvent is a solvent that will dissolve and stabilize dipolar or charged solutes, and a nonpolar solvent is a solvent that will dissolve nonpolar solutes. Since ionic liquids are salts, it is widely considered that they will provide highly polar solvents that will be suitable for dissolving polar compounds. Accordingly, phosphonium salts find utility as solvents for polar compounds. For example, phosphonium salts can dissolve many metal catalysts and some water.

It is an unexpected finding that ionic liquids that have a tetrahydrocarbylphosphonium cation can dissolve saturated hydrocarbons, which are nonpolar.

The solvent properties of phosphonium salts can be affected by the presence of dissolved water. Addition of water to a homogeneous mixture of a phosphonium ionic liquid and a hydrocarbon may result in the formation of three phases, namely, a lower water phase, an intermediate ionic liquid phase and an upper hydrocarbon phase. These can be separated for example, by decantation. For example, addition of an effective amount of water to a homogeneous solution of octane and trihexyl(tetradecyl)phosphonium chloride causes separation of the system into three phases, namely: the octane as the lightest phase; the phosphonium salt ionic liquid as the intermediate phase; and water as the heaviest phase.

It is possible that the separated ionic liquid phase may still contain some hydrocarbon. This can be removed by, for example, distillation or by one or more further steps of addition of water. It is also possible that the separated hydrocarbon phase may contain some ionic

liquid, and one or more further steps of addition of water can be carried out to separate the ionic liquid. The ionic liquid thus obtained can be purified for example by vacuum distillation at a temperature in the range from 60° to 90°C.

5 Ionic liquid has been used and recovered in this manner three times without any loss of activity.

The process for expelling a hydrocarbon from solution by addition of water may not be confined to saturated hydrocarbons, but may extend to aliphatic  
10 hydrocarbons with a modest degree of unsaturation, say a long chain olefin with only one double bond, for example heptadecene. The ability to achieve separation upon addition of water will depend on the properties of the solute and the phosphonium salt and some unsaturated  
15 hydrocarbons may react to the presence of water in a manner similar to unsaturated hydrocarbons. Not all homogeneous solutions of a hydrocarbon and a phosphonium salt may be capable of separation by addition of water. For example, addition of water to a homogeneous solution of octene and  
20 trihexyl(tetradecyl)phosphonium chloride does not cause separation into three phases: the octene remains dissolved in the phosphonium salt. However, the ability to achieve separation by addition of water can be determined for any particular combination of a phosphonium salt and a  
25 hydrocarbon by routine experimentation, without the exercise of any inventive faculty, because phase separation is readily observed by eye.

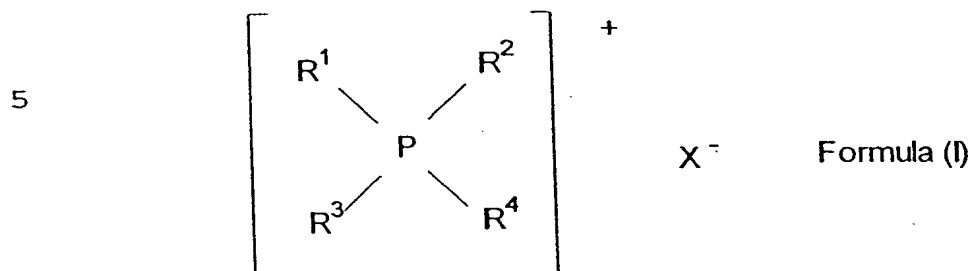
To form a homogeneous mixture, little or no water should be present in a mixture of a phosphonium salt and a  
30 hydrocarbon, especially a saturated hydrocarbon. If required, the water content of a phosphonium salt can be reduced by, for example, vacuum stripping prior to admixing

with the hydrocarbon. Vacuum stripping may be carried out at elevated temperatures and under reduced pressure, for example at 130-140° C and less than 50 mm Hg. The water content of phosphonium salts thus treated can be reduced to less than 1%, usually less than 0.2%. The phosphonium salt can be kept under a dry or inert atmosphere to maintain low moisture content. For certain applications, an inert atmosphere will be preferred.

The fact that hydrocarbons, especially saturated hydrocarbons, will dissolve in phosphonium ionic liquids provides opportunities for carrying out reactions in the ionic liquids as solvents. This is valuable as many metal catalysts are soluble in the ionic liquids, although reactions that are not catalysed and reactions that are catalysed by heterogeneous catalysts and solid state catalysts can take advantage of the solubility of the hydrocarbons in the ionic liquid. In some instances the product of reaction can be separated from the ionic liquid by the addition of water, resulting in the formation of three phases, as discussed above. In instances where addition of water is not suitable the product can be separated by other means, for example distillation. As examples of reactions there are mentioned hydrogenation, oxidation, and dimerization and oligomerization of olefinic compounds, possibly in the presence of transition metal catalysts. The property of miscibility of saturated hydrocarbons can be helpful to carry out C-H activation (see Periana et al., Science, 1998, 280, 560, incorporated herein by reference).

The phosphonium salts are tetrahydrocarbylphosphonium salts that can have a broad range of phosphonium cations and a broad range of anions.

There can be used phosphonium salts that have the general formula (I):



wherein:

10 each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently a hydrocarbyl group; and

$X^-$  is an anion; suitable anions include, for example, halides, phosphinates, alkylphosphinates, alkylthiophosphinates, sulphonates, tosylates, aluminates, borates, arsenates, cuprates, sulfates, nitrates, and carboxylates, for example acetate, decanoate, citrate and tartrate.

Tetrahydrocarbylphosphonium salts are preferred in which each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently an alkyl group of 1 to 30 carbon atoms, a cycloalkyl group of 3 to 7 carbon atoms, an alkenyl group of 2 to 30 carbon atoms, an alkynyl group of 2 to 30 carbon atoms, an aryl group of 6 to 18 carbon atoms, or an aralkyl group. It is possible for two of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  together to form an alkylene chain.

25 More preferred are phosphonium salts wherein at least one of  $R^1$  to  $R^4$  contains a higher number of carbon atoms than the other of  $R^1$  to  $R^4$ , for example 10 or more and



preferably 14 or more. There is no theoretical upper limit to the number of carbon atoms in each alkyl group, but it is contemplated that usually each alkyl group will not have more than 20 carbon atoms. Alkyl groups with 4 carbon atoms or less can lead to an increase in the melting point of the 5 ionic liquid. Therefore, for many applications, more preferred are phosphonium salts wherein each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently an alkyl group of 4 to 20 carbon atoms. For example,  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  may be n-butyl, 10 isobutyl, n-pentyl, cyclopentyl, isopentyl, n-hexyl, cyclohexyl, (2,4,4'-trimethyl)pentyl, cyclooctyl, tetradecyl, etc. Usually the total number of carbon atoms present in the phosphonium cation will not exceed 60, and preferably will not exceed 55.

15 In many cases, it is desired that  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  shall not all be identical, and that one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  shall contain a significantly higher number of carbon atoms than the others of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$ . Phosphonium salts in which  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are not identical are referred to 20 herein as asymmetric. The degree of asymmetry and the degree of branching of the hydrocarbyl groups are determinants of the melting point of the phosphonium salt: the melting point tends to decrease as the degree of asymmetry and the degree of branching are increased.

25 Therefore, for many purposes, preferred compounds are those in which  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are not identical and/or are branched. For many purposes, it is not necessary for the phosphonium salt to be liquid at room temperature to practice the current invention. Phosphonium salts that melt 30 at low temperatures, for example at temperatures less than 150° C and preferably less than 100° C, are suitable for applications that are carried out at slightly elevated

temperatures (i.e. above the melting point of the phosphonium salt).

For many applications, phosphonium salts that are water-immiscible will be preferred. The term "water  
5 immiscible" is intended to describe phosphonium salts that form a two phase system when mixed with water but does not exclude phosphonium salts that dissolve in water nor phosphonium salts that will dissolve water, provided that the two phase system forms. Phosphonium salts that have a  
10 large total number of carbons, for example equal to or greater than 20 and in particular greater than 25 or 26, or have at least one aryl group are more hydrophobic. Water immiscibility is a desirable feature of phosphonium salts because it facilitates isolation and recovery of the  
15 phosphonium salt and any dissolved catalyst.

For many applications, phosphonium salts that are less hygroscopic will be preferred. Phosphonium cations that have a larger total number of carbons, for example equal to or greater than 30 carbons and especially greater  
20 than 32 carbons, are more hydrophobic and less hygroscopic. Some anions are hygroscopic, for example chloroaluminate.

Phosphonium salts include compounds according to formula (I) wherein any of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently an aryl or arylalkyl group. For example, one or more of  $R^1$ ,  
25  $R^2$ ,  $R^3$  and  $R^4$  may be phenyl, phenethyl, toluyyl, xylyl, or naphthyl.

It is possible for the groups  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  to bear substituents, or to include heteroatoms, provided that the substituents or heteroatoms do not adversely affect the  
30 desired properties of the compound. Acceptable substituents include alkoxy, alkylthio, acetyl, and hydroxyl groups, and

acceptable heteroatoms include oxygen and sulphur. Since substituents and heteroatoms are likely to increase the cost of the phosphonium compound, it is contemplated that, for the most part, substituents and heteroatoms will not be present.

$X^-$  can be any anion that can form a liquid salt at temperatures below about 150° C with a cation described above. Anions that form liquids at temperatures below about 100° C are more preferred, and those that form liquids below about 80° C are still more preferred. Suitable anions include, for example: halides, especially chlorides and bromides; phosphinates; phosphates; mono- and dialkylphosphinates, for example diisobutylphosphinate and bis(2,4,4'-trimethylpentyl)phosphinate, dicyclohexylphosphinate; alkylthiophosphinates, for example, diisobutyldithiophosphinate; sulphonates; tosylates; aluminates; borates; arsenates; cuprates; sulfates; nitrates; triflates; bis(trifluoromethylsulfonyl)amides; camphorsulfonates; perchlorates; citrates; tartarates; phenoxides; alkoxides; tetrachlorometalates; C2 to C20 alkanoates and alkenoates, such as acetate, decanoate, oleate, palmitate and stearate; perfluoroalkanoates; tetrafluoroborates; hexafluorophosphates; tris(trifluoromethylsulfonyl)methides and sulphur analogues; hexafluorophosphate; hexafluoroantimonate; hexafluoroarsenate; trifluoromethylsulphonate; fluorosulphonate; tetrachloroaluminate; dichlorocuprate; trichlorocuprate; tetrachlorocuprate; heptachloroaluminate; decachloroaluminate; heptachloroaluminate; and trichlorozincate.

The anion can have some effect on miscibility of the phosphonium salt and saturated hydrocarbons. For

example, anions that contain alkyl groups with a large total number of carbon atoms will increase the hydrophobicity of the phosphonium salt and may be preferred in some applications. Of those anions that contain alkyl groups, 5 the alkyl groups each independently may have any of the values given to  $R^1$  to  $R^4$  of the phosphonium cation (as defined above).

Some of the phosphonium compounds of formula I are novel. For example compounds with hydrocarbylphosphinate 10 and hydrocarbylthiophosphinate anions are novel and are the subject of Canadian Patent Application Serial No. 2,343,456, filed March 30, 2001. Novel compounds of formula I can be obtained, for example from compounds of formula I in which the anion is a good leaving group, for example a halide, 15 especially chloride or bromide, or sulfate by ion exchange reaction with a corresponding salt containing the required anion. Ammonium or alkali metal salts of the required anion can be used for the ion exchange reaction.

The anion of the tetrahydrocarbylphosphonium salt 20 may affect the chemical properties, reactivity profile, thermodynamic properties and physical properties of the phosphonium salt ionic liquid. Therefore, certain anions may be preferred for certain applications, as illustrated in the following examples:

25 (i) Many of the phosphonium tetrafluoroborates and hexafluorophosphates are liquids at room temperature and are therefore suitable for room-temperature reactions.

(ii) For some applications,  $X^-$  is preferably not a halide. Halide ions, especially chloride ions, can 30 coordinate with some catalysts, for example catalysts containing metals of group VIII of the periodic table (i.e.

palladium), and reduce catalytic activity. Halide ions should not be used where there is concern regarding reducing catalytic activity, but can be used in other applications. Phosphonium salts having halide ions can be used in the  
5 preparation of ionic liquids having other anions, for example acetate, trifluoroacetate, nitrate, bis(trifluoromethylsulfonyl)imide and triflate ions. This can be done by ion exchange, for example in acetone, with stirring at 0° to 60° C.

10 (iii) Phosphinate,  
tris(trifluoromethylsulfonyl)imide and triflate anions may provide enhanced catalytic activity for some applications.

(iv) Moisture sensitive anions will not be practical for some applications, especially those that  
15 involve addition of water, for example to effect separation of saturated hydrocarbons from the phosphonium salt. Moisture sensitive anions include metal halides, for example: tetrachloroaluminate, and transition metal halides such as tetrachloroferrate, or trichlorocuprate.

20 (v) Trihexyl(tetradecyl)phosphonium  
bis(trifluoromethylsulfonyl)imide has low viscosity and is stable in the presence of 100% nitric acid, for example at temperatures in the range of 20-80° C for a duration of at least three days. Therefore, the  
25 bis(trifluoromethylsulfonyl)imide anion may be preferred for applications involving nitric acid or oxidants (such as peroxides, molecular oxygen and air) and/or for applications in which low viscosity is desirable.

(vi) Preferred anions for acid catalysis reactions  
30 such as sulfonation, Friedel-Crafts alkylation, acylations using super acidic acid catalysts (zeolite, metal triflates,

metal triflamides, clays, etc.) include:  
bis(trifluoromethylsulfonyl)imide and triflate.

The following list provides examples of preferred  
phosphonium salts:

- 5 trihexyl(tetradecyl)phosphonium chloride;  
tripentyl(tetradecyl)phosphonium chloride;  
trioctyl(tetradecyl)phosphonium chloride;  
trihexyl(tetradecyl)phosphonium bromide;  
trihexyl(tetradecyl)phosphonium  
10 bis(trifluoromethylsulfonyl)imide;  
trihexyl(tetradecyl)phosphonium  
dicyclohexylphosphinate;  
trihexyl(tetradecyl)phosphonium tetrafluoroborate;  
trihexyl(tetradecyl)phosphonium decanoate;  
15 trihexyl(tetradecyl)phosphonium triflate;  
trihexyl(tetradecyl)phosphonium  
tris(trifluoromethylsulfonyl)imide;  
trihexyl(tetradecyl)phosphonium  
tris(trifluoromethylsulfonyl)methide; and  
20 triisobutyl(tetradecyl)(methyl)phosphonium  
tosylate.

Saturated hydrocarbons present in homogeneous  
mixtures can be straight chained, branched, or cyclic  
aliphatic molecules. There is no theoretical upper limit to  
25 the number of carbon atoms in the saturated hydrocarbon.  
However, saturated hydrocarbons with large numbers of carbon

atoms exist in the solid phase at ambient temperatures, and accordingly, slightly elevated temperatures (for example, temperatures in the range of about 30-100° C) may be required in order to dissolve a saturated hydrocarbon with a large  
5 number of carbon atoms in a phosphonium salt. The saturated hydrocarbons may have as few as one carbon atom. There is no particular upper limit on the number of carbon atoms, but most interest is in those having up to about 20 carbon atoms. Saturated hydrocarbon compounds containing a low  
10 number of carbon atoms have low boiling points, so it may be necessary to apply pressure in order to obtain homogeneous mixtures of the saturated hydrocarbon and phosphonium salt.

Examples of saturated hydrocarbons include alkanes and cycloalkanes, for example: methane, ethane, propane,  
15 isopropane, butane, isobutane, pentane, hexane, cyclohexane, heptane, octane, nonane, and eicosane. The foregoing list provides examples only and the invention is not restricted to these compounds. Mixtures of hydrocarbons can of course be used. Commercially available mixtures include "petroleum  
20 ether" (b.p. 45°C to 60°C), which comprises a mixture of butanes, pentanes and hexanes.

Homogeneous mixtures of saturated hydrocarbons and phosphonium salts according to the current invention find utility in reactions involving saturated hydrocarbons. For  
25 example, saturated hydrocarbons in the homogeneous mixtures can be reacted with activated halogen to produce alkyl halides; the halogen may be activated by known methods known in the art, for example light, heat, or a suitable catalyst such as a ferric salt. The alkyl halides thus obtained can  
30 be further substituted (i.e. functionalized) using any of a number of substitution reactions known to those skilled in the art. For example, alkyl halides may be converted to:

alcohols by reaction with water (hydrolysis);

ethers by reaction with an alkali metal alkoxide,  
such as sodium alkoxide;

amines by reaction with ammonia;

5           mercaptans by reaction with an alkali metal  
sulfide, such as sodium sulfide; or

nitroalkanes by treatment with an alkali metal  
nitrite, such as sodium nitrite.

The foregoing list of reactions is illustrative and is not  
10 limiting. Examples of suitable reactions include  
substitution of methane or ethane with a halogen followed by  
hydrolysis to produce methanol and ethanol, respectively.

In many cases, the preferred process for recovery  
of reaction products from the reaction mixture will be  
15 distillation, especially under reduced pressure. Reaction  
products can be isolated from the reaction mixture by  
distillation because the vapour pressure of phosphonium salt  
ionic liquids is extremely low. Distillation is suitable  
for recovery of polar products such as methanol and ethanol.

20           In a further embodiment, a homogeneous mixture  
comprising a saturated hydrocarbon and a phosphonium salt  
may find utility as a stable reservoir for a hydrocarbon or  
a mixture of hydrocarbons, especially for saturated  
hydrocarbon gases or saturated hydrocarbons that have low  
25 flash points. For example, a saturated hydrocarbon will  
have a lower vapour pressure and therefore a lower flash  
point when dissolved in a phosphonium salt. As a result, a  
homogeneous mixture of a saturated hydrocarbon and a  
phosphonium salt will be more easily contained and more  
30 conveniently and safely shipped and handled than a pure



saturated hydrocarbon. Thus, the phosphonium salt may find utility as a stabilizer or flame retardant for saturated hydrocarbons.

The current invention further provides a means of  
5 extracting hydrocarbons from a source of hydrocarbons (such as coal, oil sands (tar sands), or oil shale) into a homogeneous solution. A phosphonium salt is contacted with the source of hydrocarbons and hydrocarbons are extracted into the phosphonium salt, thereby forming a homogeneous  
10 mixture comprising hydrocarbons and phosphonium salt. The resulting homogeneous mixture may comprise any hydrocarbons that were contained in the source, including saturated and unsaturated hydrocarbons as well as aromatic compounds. Therefore, the homogeneous mixture may comprise a crude  
15 extract of a mixture of hydrocarbons. The homogeneous mixture can be separated from any remaining solid material, for example by filtering. The extracted hydrocarbons may be purified from the crude extract, for example by fractional distillation. However, it may be desirable to use the crude  
20 extract of hydrocarbons in phosphonium salt directly in certain reactions, such as cracking. In either crude extract or purified form, the extracted hydrocarbons find utility in several commercially important reactions, including catalytic hydrogenation (both addition  
25 hydrogenation and destructive hydrogenation or hydrogenolysis), cracking, gasification, methanation, and various substitution and functionalization reactions, for example halogenation.

The separation effected by addition of water may  
30 rely on the ability of the phosphonium salt to dissolve enough water to effect phase separation of the hydrocarbon. The minimum amount of water required to achieve phase separation is readily observed by eye and may be as little

as 5% w/v (water in phosphonium salt) or as much as 15% w/v (water in phosphonium salt) and will depend on the particular phosphonium salt and also on the particular hydrocarbon, but it can be determined for any particular salt and hydrocarbon by routine experimentation without exercise of any inventive faculty. The amount of water required to effect separation may be more than, the same as, or less than the amount of water that can dissolve in the particular phosphonium salt.

10           Phosphonium salts that are more hydrophobic, i.e. contain a larger total number of carbon atoms, will dissolve less water. Therefore, if phase separation is to be achieved by addition of water, there may be an upper limit to the total number of carbon atoms that may be present in the phosphonium salt. Therefore, phosphonium salts wherein  
15           the cation contains equal to or less than 60 and preferably less than 55 carbon atoms are more preferred. More polar phosphonium salts may require a smaller minimum amount of water to be added to effect phase separation, even though  
20           they are capable of dissolving larger quantities of water.

          Addition of water in excess of the amount that can be dissolved in a phosphonium salt that is immiscible with water will result in formation of a new phase, namely an aqueous phase. By way of illustration,  
25           trihexyl(tetradecyl)phosphonium chloride becomes saturated with water at about 10-15% w/v water content, and addition of water in excess of this amount results in the formation of a separate aqueous phase.

          The separation effected by addition of water also  
30           may rely on the properties of the hydrocarbon solute. Hydrocarbons that are nonpolar or have a low degree of polarity or are hydrophobic are more likely to be expelled

from a phosphonium salt upon addition of water. Therefore, saturated hydrocarbons are preferred. Also mentioned are unsaturated hydrocarbons with a low degree of unsaturation and a large number of carbon atoms, say 10 or more.

5 Examples of unsaturated hydrocarbons that may separate from solution upon addition of water include: octene, tetradecene, heptadecene, eicosene and eicodiene. Whether a particular olefin will separate may depend upon the particular phosphonium salt, as well as upon the olefin.

10 Separation of a hydrocarbon by addition of water finds utility in recovering products of certain reactions. Mention is made of the hydrogenation of unsaturated hydrocarbons (including olefins, alkynes and arenes) to produce saturated hydrocarbons. An unsaturated hydrocarbon  
15 and a suitable metal catalyst (for example, palladium acetate) are dissolved in a phosphonium salt solvent to produce a homogeneous mixture. Hydrogen gas is supplied to the reaction mixture and, upon completion of the reaction, the saturated hydrocarbon reaction product can be recovered  
20 by adding water to the reaction mixture, thereby causing the saturated hydrocarbon reaction product to separate from the solvent and form an upper phase that can be decanted and thus isolated from the remaining reaction mixture. The olefins can be monoolefins or diolefins, including  
25 conjugated and unconjugated diolefins. Other compounds that can be hydrogenated include acetylenic compounds, and aromatic hydrocarbons (in particular, polynuclear aromatic hydrocarbons). Examples of suitable olefins include: butenes, pentenes, butadiene, isoprene, and 1,5-  
30 cyclooctadiene.

Mention is also made of reactions in which olefins are dimerized, oligomerized or polymerized and, if required, subsequently hydrogenated to form higher alkanes. In a

typical reaction, an olefin can be dimerized or oligomerized and subsequently hydrogenated using standard transition metal catalysis chemistry and phosphonium salt solvents, and the higher alkanes produced can be recovered from the  
5 reaction mixture by adding water to effect phase separation and decanting the saturated hydrocarbon layer. For example, butene can be dimerized and hydrogenated to obtain octane and the octane can be recovered from the reaction mixture by addition of water to effect phase separation. Or, isoprene  
10 can be oligomerized to produce terpenes, which may be recovered from the reaction mixture by addition of water to effect phase separation.

For some applications, a suitable catalyst will be dissolved in the phosphonium salt along with the hydrocarbon  
15 reagent. However, solid-state catalysts and supported catalysts may be used. Examples of catalysts for hydrogenation of olefins can be found in U.S. Patent 5,852,130. These catalysts include zero-, mono-, di-, and trivalent compounds in which the metal is selected from the  
20 group consisting of Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, and Pt, and can be bonded to a suitable ion, for example halide, hexafluorophosphate, hexafluoroarsenate, tetrafluoroborate, tetrachloroborate, or to a suitable hydrocarbon ligand such as cyclopentadienyl and substituted cyclopentadienyl,  
25 acetylacetonate and substituted acetylacetonate, or to a suitable neutral ligand such as tertiary phosphine, ditertiary diphosphine, phosphite, olefin, carbon monoxide, or nitrile. These complexes may be mononuclear or polynuclear, neutral, or ionic. They may contain a chiral  
30 ligand.

#### EXAMPLES:

##### Example 1:

6 ml of octane was added to 3 ml of trihexyl(tetradecyl)phosphonium chloride at room temperature under atmospheric pressure. A single phase was obtained, consisting of a homogeneous mixture of the octane and  
5 solvent.

1.2 ml of water were added to the octane/solvent mixture with stirring. Stirring was stopped and the system was allowed to settle. The system settled into three distinct phases: a lower aqueous phase, a middle  
10 trihexyl(tetradecyl)phosphonium chloride phase, and an upper octane phase.

The upper octane phase was decanted. Recovery of octane was essentially quantitative.

The trihexyl(tetradecyl)phosphonium chloride phase  
15 was then decanted and subsequently dried by vacuum stripping at 130° C and about 50 mm Hg. The recovery of trihexyl(tetradecyl)phosphonium chloride was essentially quantitative.

Example 2:

20 1 g of octene was added to 1 g of trihexyl(tetradecyl)phosphonium chloride at room temperature, under atmospheric pressure. A single phase was obtained, consisting of a homogeneous mixture of the octene and solvent.

25 1 g of water was added to the octene/solvent mixture with stirring. Stirring was stopped and the system was allowed to settle. The system settled into two distinct phases: a single upper phase consisting of octene and trihexyl(tetradecyl)phosphonium chloride, and an aqueous  
30 lower phase.

CLAIMS:

1. A homogeneous mixture comprising a saturated hydrocarbon and a tetrahydrocarbylphosphonium salt.
2. A homogeneous mixture according to claim 1,  
5 wherein the tetrahydrocarbylphosphonium salt is immiscible with water.
3. A homogeneous mixture according to claim 2, wherein the tetrahydrocarbylphosphonium salt is selected from the group consisting of:  
10 trihexyl(tetradecyl)phosphonium chloride;  
tripentyl(tetradecyl)phosphonium chloride;  
trioctyl(tetradecyl)phosphonium chloride;  
trihexyl(tetradecyl)phosphonium bromide;  
trihexyl(tetradecyl)phosphonium  
15 bis(trifluoromethylsulfonyl)imide;  
trihexyl(tetradecyl)phosphonium  
dicyclohexylphosphinate;  
trihexyl(tetradecyl)phosphonium tetrafluoroborate;  
trihexyl(tetradecyl)phosphonium decanoate;  
20 trihexyl(tetradecyl)phosphonium triflate;  
trihexyl(tetradecyl)phosphonium tris(trifluoro-  
methylsulfonyl)methide; and  
triisobutyl(tetradecyl)(methyl)phosphonium  
tosylate.

4. A homogeneous mixture according to any one of claims 1 to 3, further comprising a metal catalyst.

5. A process for expelling a hydrocarbon from a homogeneous mixture comprising the hydrocarbon and a tetrahydrocarbylphosphonium salt ionic liquid, which process comprises adding to the homogeneous mixture sufficient water to cause the hydrocarbon and the tetrahydrocarbylphosphonium salt ionic liquid to form separate phases.

6. A process according to claim 5, wherein the hydrocarbon is a saturated hydrocarbon.

7. A process according to claim 5 or 6, wherein the tetrahydrocarbylphosphonium salt ionic liquid is immiscible with water.

8. A process according to claim 5, 6, or 7 wherein the tetrahydrocarbylphosphonium salt is selected from the group consisting of:

trihexyl(tetradecyl)phosphonium chloride;

tripentyl(tetradecyl)phosphonium chloride;

trioctyl(tetradecyl)phosphonium chloride;

trihexyl(tetradecyl)phosphonium bromide;

trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide;

trihexyl(tetradecyl)phosphonium dicyclohexylphosphinate;

trihexyl(tetradecyl)phosphonium tetrafluoroborate;

trihexyl(tetradecyl)phosphonium decanoate;

trihexyl(tetradecyl)phosphonium triflate;

trihexyl(tetradecyl)phosphonium tris(trifluoromethylsulfonyl)methide; and

5 triisobutyl(tetradecyl)(methyl)phosphonium  
tosylate.

9. A three phase system comprising a hydrocarbon phase, a tetrahydrocarbylphosphonium salt ionic liquid phase, and a water phase.

10. A three phase system according to claim 9, wherein  
10 the hydrocarbon is a saturated hydrocarbon.

11. A three phase system according to claim 9, wherein the tetrahydrocarbylphosphonium salt ionic liquid is water immiscible.

12. Use of a tetrahydrocarbylphosphonium salt as a  
15 solvent for a saturated hydrocarbon.

12. A method for extracting hydrocarbons from a source of hydrocarbons into a homogeneous solution, the method comprising contacting a tetrahydrocarbylphosphonium salt with the source of hydrocarbons so as to extract  
20 hydrocarbons in the tetrahydrocarbylphosphonium salt and produce a homogeneous solution comprising hydrocarbons and the tetrahydrocarbylphosphonium salt.



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/25990

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K3/00 C07C9/00 C07F9/54

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C07F C10G C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 707 501 A (GENTIT ET AL) 26 December 1972 (1972-12-26) column 7, line 66 - line 71 column 2, paragraph 1 ---	1
A	US 4 359 596 A (HOWARD KENT A ET AL) 16 November 1982 (1982-11-16) -----	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

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Information on patent family members

In International Application No

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